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THIOPHENE ACETYLENES FROM *LEUZEA* ROOTS*

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Key Word Index—*Leuzea carthamoides*; Compositae; thiophene acetylenes.

Abstract—The isolation and identification of four polyacetylenes is reported from the roots of *Leuzea carthamoides*. The compounds belong to a uniform series of thiophene acetylenes; two of the compounds are new, whereas two are already known.

INTRODUCTION

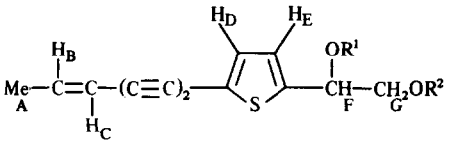
Crude or partially purified aqueous and alcoholic extracts prepared from the roots of *Leuzea carthamoides* DC (syn. *Rhaponticum carthamoides* Willd. Iljin) have been used for some time as stimulants, roborants and tonics [1, 2]. The crude drug 'Rhizoma cum radicibus Leuzeae' has been officially recognized in the last two editions of the Russian Pharmacopoeia [3, 4] and the plant is now being cultivated and processed for human and veterinarian use [5–7]. Although preparations and some evidence for the stimulant activity existed as early as 1952 [2], only a few attempts have, until now, been made to characterize the chemical principles present in the plant or its extracts. These sporadic studies indicated the presence of uncharacterized saponins [8], simple flavonols, a flavone [9, 10] and ecdysteroids [11, 12]. The latter compounds were suggested to be responsible for the reputed roborant activity of the plant [13].

A recent paper of Savina *et al.* [14] indicated that polyacetylene-type compounds may be present in abundant amounts in the roots. Since the tribe Cynareae is extremely rich in various types of polyacetylenes [15, 16], we have investigated *Leuzea* roots specifically for the presence of polyacetylenes.

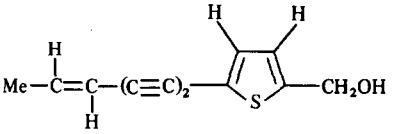
RESULTS AND DISCUSSION

TLC analysis of the benzene extract revealed that six components were present in substantial amounts besides a series of terpenoid-type compounds. They were separated by usual chromatographic techniques [17] and structures **1**, **3**, **4** and **6** were assigned to four of them on the basis of their spectral characteristics and simple conversions (see Fig. 1). Scarcity of material of one compound (L/BP/2) prevented complete structural studies and one product (an unusual mixture of four isomers) will be dealt with separately.

Thus, compound **1** proved to be identical with the polyacetylene isolated from the same source by Savina *et al.* [14]. The thiophene and the corresponding diol **6** have been found also in related genera, like *Serratula* [18] and *Saussurea* [19]. The new compounds **3** and **4** could easily have been artefacts originating from the above compounds. This possibility was ruled out by a careful TLC analysis of the methanolic extract prepared from fresh plant material. On the other hand, each compound was detected also in *L. galenic* preparations (tinctura and extractum liquidum) in the same relative quantities as in the plant material. They can, therefore, be considered as characteristic chemical markers in the analytical protocol as well as in the standardization procedure.



	R^1	R^2
1	Ac	Ac
4	H	Ac
6	H	H



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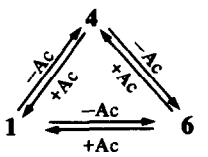

Fig. 1.

*Part 2 in the series "Leuzea polyacetylenes". For part 1 see ref. [17].

Table 1. ^{1}H NMR spectral data of compounds **1**, **3**, **4** and **6** (90 MHz, $CDCl_3$, TMS int. standard)

H	1	3	4	6
A	1.90	1.88	1.9	1.85
B	*ca* 6.30	6.37	6.39	6.34
C	5.60	5.61	5.61	5.54
D	6.93	6.86	6.87	6.82
E	7.15	7.15	7.16	7.15
F	*ca* 6.20	4.78	5.15	4.89
G	4.39	—	4.33	3.73
Ac	2.12	—	2.15	—
	2.14	—	—	—

EXPERIMENTAL

Plant material was supplied by the University of Horticultural Sciences, Budapest. Reference sample and voucher specimens are available at the same source. Extraction and isolation procedures were published in detail in ref. [17].

Compound **1**. Yellow oil, UV λ_{max}^{MeOH} nm: 217, 256, 261, 270, 302sh, 322, 344sh; IR ν_{max}^{KBr} cm^{-1}: 2960, 2200, 2140, 1755, 1422, 1370, 1226, 1049, 950, 870, 810; MS *m/z* (rel. int.): 316 $[M]^+$ (41), (256) $[M-AcOH]^+$ (55), 214 $[M-AcOH-CH_2CO]^+$ (100), 201 $[M-Me-CH_2CO]^+$ (82), 171 $[M-CH(COOMe)-CH_2COOMe]^+$ (9); ^{1}H NMR: Table 1.

Compound L/BP/2. Yellow oil; UV λ_{max}^{MeOH} nm: 215, 249, 267, 280, 298, 316, 338; IR ν_{max}^{KBr} cm^{-1}: 3450, 2940, 2880, 2380, 2230, 1755, 1645, 1630, 1380, 1250, 1138, 1110, 989, 955, 880.

Compound **3**. Cream crystals, mp 72–75°; UV λ_{max}^{MeOH} nm: 217, 227sh, 256, 261, 271, 304sh, 321, 348sh; IR ν_{max}^{KBr} cm^{-1}: 3260, 2900, 2210, 2150, 1613, 1440, 1362, 1349, 1285, 1182, 1130, 1030, 995, 942, 805; MS *m/z* (rel. int.): 202 $[M]^+$ (100) 185 $[M-H_2O]^+$ (46), 174 $[M-CO]^+$ (16), 171 $[M-CH_2OH]^+$ (20) . . .; ^{1}H NMR: Table 1.

Compound **4**. Cream crystals, mp 82–84°; UV λ_{max}^{MeOH} nm: 217, 226sh, 257, 270, 303sh, 324, 346sh; IR ν_{max}^{KBr} cm^{-1}: 3310, 2940, 2885, 2170, 2210, 1700, 1430, 1385, 1360, 1270, 1235, 1225, 1185, 1145, 1080, 1035, 980, 944, 895, 802; MS *m/z* (rel. int.): 274 $[M]^+$ (15), 256 $[M-H_2O]^+$ (2), 214 $[M-HOAc]^+$ (70), 201 $[M-CH_2COOMe]^+$ (100), 185 $[M-C_7H_5]^+$ (12), 171 $[M-CH(OH)-CH_2COOMe]^+$ (28) . . .; ^{1}H NMR: Table 1.

Compound **6**. Cream crystals, mp 96–98°; UV λ_{max}^{MeOH} nm: 217, 255, 270, 304sh, 321, 346sh; IR ν_{max}^{KBr} cm^{-1}: 3200 (*br*), 2870, 2160, 2100, 1610 w, 1435, 1285, 1200, 1160, 1090, 1055, 1040, 940, 875, 810; MS *m/z* (rel. int.): 232 $[M]^+$ (25), 201 $[M-CH_2OH]^+$ (100), 171 $[M-CH(OH)-CH_2OH]^+$ . . .; ^{1}H NMR: Table 1.

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